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The geomycology of elemental cycling and transformations in the environment

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SUMMARY

Geomicrobiology addresses the roles of microorganisms in geological and geochemical processes and geomycology is a part of this topic focussing on the fungi. Geoactive roles of fungi include organic and inorganic transformations important in nutrient and element cycling, rock and mineral bioweathering, mycogenic biomineral formation, and metal-fungal interactions. Lichens and mycorrhizas are significant geoactive agents. Organic matter decomposition is important for cycling of major biomass-associated elements, e.g. C, H, N, O, P and S as well as all other elements found in lower concentrations. Transformations of metals and minerals are central to geomicrobiology, and fungi effect changes in metal speciation, as well as mediate mineral formation or dissolution. Such mechanisms are components of biogeochemical cycles for metals as well as associated elements in biomass, soil, rocks and minerals, e.g. S, P, and metalloids. Fungi may have the greatest geochemical influence within the terrestrial environment. However, they are also important in the aquatic environment and significant components of the deep subsurface, extreme environments and habitats polluted by xenobiotics, metals and radionuclides. Applications of geomycology include metal and radionuclide bioleaching, biorecovery, detoxification, and bioremediation, and the production of biominerals or metal(loid) elements with catalytic or other properties. Adverse effects include biodeterioration of natural and synthetic materials, rock and mineral-based building materials (e.g. concrete), cultural heritage, metals, alloys and related substances, and adverse effects on radionuclide mobility and containment. The ubiquity and importance of fungi in the biosphere underlines the importance of geomycology as a conceptual framework encompassing the environmental activities of fungi.

INTRODUCTION

The significance of fungi in natural environments is extensive and profound. Their most obvious roles are as decomposers of organic materials, and as animal and plant pathogens and symbionts. It is therefore obvious that they are of major importance in the global carbon cycle through such activities and as important determinants of plant growth and productivity. However, their importance in terms of nutrient and element cycling greatly extends beyond this core activity and they are involved in the biogeochemical cycling of many other elements and substances, as well as many other related processes of environmental significance. The growing discipline of geomicrobiology addresses the roles of microorganisms in geological and geochemical processes (1,2), and geomycology can be considered to be a part of this topic that focusses on the fungi (3,4). The often clear demarcation between mycological and bacteriological research has ensured that the geoactive properties and significance of fungi have been unappreciated in wider geomicrobiological contexts. The range of prokaryotic metabolic diversity found in archaea and bacteria, including their abilities to use a variety of different terminal electron acceptors in respiration and effect redox transformations of many metal species (5,6), has also contributed to a narrow overall view of the significance of eukaryotic organisms in important biosphere processes. A recent collection of geomicrobiology review articles managed to completely exclude fungi (as well as algae), even to the extent of defining “microbes” as being only bacteria and archaea (7). Nevertheless, appreciation of fungi as agents of geochemical change is growing, and their significance is being discovered even in locations not usually regarded as prime fungal habitats, e.g. rocks, acid mine drainage, deep aquatic sediments, hydrothermal vents and the igneous oceanic crust (8-11). Their significance as bioweathering agents of rocks and minerals is probably better understood than bacterial roles (12), and this ability is of prime importance in the weathering of human structures in the built environment and cultural heritage (13-15). On the positive side, the geoactive properties of fungi can be used for

human benefit and several aspects may contribute to providing solutions to several important global challenges. Geomycology is relevant to reclamation and revegetation of polluted habitats, bioremediation, nuclear decommissioning and radionuclide containment, biorecovery of important elements, and the production of novel biomaterials. This chapter outlines important geoactive properties of fungi in relation to important environmental processes, their positive and negative applications and impact on human society.

THE FUNGAL HABITAT

Fungi are ubiquitous components of the microbial communities of any terrestrial environment, including such hostile habitats as the Arctic, hot deserts, and metal-rich and hypersaline soils (16). They are significant inhabitants of the aquatic environment as decomposers of organic matter but are also involved in other elemental cycles, e.g. Manganese oxidation (17). Fungi are ubiquitous in habitats polluted by xenobiotics, toxic metals and radionuclides, both terrestrial and aquatic, as well as leachates and other solid or liquid wastes (18). In such habitats, fungi may exhibit a variety of mechanisms that determine tolerance and survival, and which are also components of elemental cycles for pollutant elements (18). These “extreme” locations may also act as a reservoir of novel organisms with unusual properties. For example, acid mine drainage is now known to harbor fungal communities, the preponderance of earlier research on this habitat being devoted to prokaryotes, and some isolates possess unusual element bioaccumulation properties. New species include *Fodinomyces uranophilus* and *Coniochaeta fodinicola* from uranium mine locations that can bind mobile uranium (10,19) and a *Penidiella* sp. from an acidic abandoned mine location that was capable of accumulating rare earth elements such as dysprosium (Dy) (20). A global fungal role in biogeochemical cycling of the elements (e.g. C, H, N, O, P, S, metals, metalloids) is therefore obvious and interlinked with the ability to adopt a variety of

growth, metabolic and morphological strategies, adaptive capabilities to environmental extremes and, their symbiotic associations with animals, plants, algae and cyanobacteria (16,21,22). The ability of many fungi to grow oligotrophically by scavenging nutrients from the air and rainwater helps them survive on stone and rock surfaces which are considered to be an inhospitable environment (9,23). In addition, organic and inorganic residues on mineral surfaces or within cracks and fissures can act as nutrient sources in the sub-aerial rock environment (24). One of the most successful means for fungi to survive in the extreme sub-aerial environment is underpinned by their symbiotic associations with algae and cyanobacteria as lichens where the phototrophs provide a source of carbon and protection from light and irradiation (24,25). Lichens enable colonization of a wide range of environments including those at climatic extremes such as the Arctic and Antarctic, exposed rock surfaces and dry deserts.

In the deep subsurface, the research emphasis is mostly on prokaryotes, but the presence of fungi is now well known (11, 26-28). Fungi occur in abundance and high diversity in such varied environments as deep-sea sediments (29), hydrothermal vents (30,31), and methane cold-seeps (29,32). They are now also known as abundant inhabitants of the igneous oceanic crust which has consequently been described as the largest fungal habitat on Earth (11). Fungi seem to play an important ecological role in the igneous oceanic crust as they exist in symbiosis with chemolithotrophic prokaryotes, decompose organic matter, dissolve and form minerals, and therefore are involved in the cycling of elements (11,33,34). Fossilized microorganisms have been observed in drilled cores and dredged samples from the ocean floor with a majority of these findings representing fungi (34,35). These fungi existed in a close symbiotic-like relationship with two types of prokaryotes, which appeared to use the structural framework of the mycelium for their growth (34). It therefore seems clear that

geomycological processes are significant in a wide range of biosphere habitats, including those traditionally thought to be inimical to fungal growth and development (36).

ORGANIC MATTER DECOMPOSITION AND BIOGEOCHEMICAL CYCLING OF COMPONENT ELEMENTS

Organic matter decomposition is the attribute most commonly associated with fungi, and is a major contribution to global biogeochemistry as well as the spoilage of foodstuffs and organic materials (21,36). In fact, fungal processes represent a potential control point in the global carbon cycle (37). To some extent, research on this aspect of chemoorganotrophic metabolism has obscured the wider global implications of decomposition in terms of the cycling of other elements and nutrients, and also contributed to a lack of attention to fungal roles in wider geochemical cycles.

Most biogeochemical attention on fungi has been given to carbon and nitrogen cycles, and the ability of fungi to utilize a wide spectrum of organic compounds is well known. Simple compounds such as sugars, organic acids, and amino acids can easily be transported into the cell while more complex molecules are first broken down to smaller molecules by extracellular enzymes before cellular entry. Such compounds include natural substances such as cellulose, pectin, lignin, lignocellulose, chitin and starch to anthropogenic products like hydrocarbons, pesticides, and other xenobiotics (21,37). Organometals (compounds with at least one metal-carbon bond) can also be attacked by fungi. Degradation of organometallic compounds can be carried out by fungi either by direct enzymic action or by facilitating abiotic degradation, e.g. by alteration of external pH through metabolite excretion. Tributyltin oxide and tributyltin naphthenate may be degraded to mono- and dibutyltins by fungal action, inorganic Sn(II) being the final degradation product (38). Organomercury compounds may be

detoxified by conversion to Hg(II) by fungal organomercury lyase, the Hg(II) being subsequently reduced to Hg(0) by mercuric reductase, a system analogous to that found in mercury-resistant bacteria.

Some fungi have remarkable degradative properties and ligninolytic fungi, like the white rot *Phanerochaete chrysosporium*, can degrade many xenobiotics including aromatic hydrocarbons, chlorinated organics, polychlorinated biphenyls, nitrogen-containing aromatics and many other pesticides, dyes and xenobiotics (39,40). Such activities are of importance in polluted habitats and have been applied in bioremediation where ligninolytic fungi have been used to treat soil contaminated with substances like pentachlorophenol (PCP) and polynuclear aromatic hydrocarbons (PAHs) (21, 41-43). In many cases, xenobiotic-transforming fungi need additional utilizable carbon sources for co-metabolism because although capable of degradation, they cannot adequately utilize these substrates as an energy source. Inexpensive utilizable lignicellulosic wastes such as corn cobs, straw and sawdust can therefore be used as nutrient additions for enhanced pollutant degradation. Wood-rotting and other fungi have also received considerable attention for the bleaching of dyes and industrial effluents, and biotreatment of various agricultural wastes such as forestry, pulp and paper by-products, sugar cane bagasse, coffee pulp, sugar beet pulp, apple and tomato pulp, and cyanide (42).

As mentioned, fungi are highly important in the degradation of naturally-occurring complex molecules in terrestrial and aquatic habitats. Since around 95% of plant tissue is composed of carbon, hydrogen, oxygen, nitrogen, phosphorus and sulfur, decomposition activities of fungi are clearly important in relation to redistribution of these elements between organisms and environmental compartments. As well as C, H, O, N, P, and S, another 15 elements are typically found in living plant tissues - K, Ca, Mg, B, Cl, Fe, Mn, Zn, Cu, Mo, Ni, Co, Se,

Na, Si. However, all 90 or so naturally-occurring elements may be found in plants, mostly at low concentrations although this may be highly dependent on environmental conditions. These include toxic and inessential metals and metalloids including As, Hg, Pb and U. Some plants accumulate relatively high concentrations of metals like Ni and Cd. Plant metal concentrations may reflect environmental conditions and provide a bioindicator of toxic metal pollution or a metalliferous substrate. Metal-accumulating plants are also receiving attention in bioremediation (=phytoremediation).

Similar concepts of element cycling also relate to animal and microbial biomass. Animals also contain multiple elements in varying amounts. The human body (like other organisms) is mostly water and around 99% of the mass comprises oxygen, carbon, hydrogen, nitrogen, calcium and phosphorus. However, many other elements are present in lower amounts including substances taken up as contaminants in food and water. It follows that decomposition, degradative and pathogenic activities of fungi are linked to the redistribution and cycling of all these constituent elements on local and global scales. There must be a fungal component therefore in the biogeochemical cycles of virtually all biomass-associated elements (3,21). The release of elements and nutrient moieties through degradation makes them available to other microorganisms and plants, and also chemical interaction with the environmental pool of different chemical species.

FUNGAL INTERACTIONS WITH THE INORGANIC ENVIRONMENT: ROCKS, MINERALS AND METALS

Bioweathering

Rocks and minerals represent a vast reservoir of elements, many essential for life, and such elements must be released in forms that may be assimilated by the biota. These include essential metals as well as elements like S and P (3,44). Many important microbial processes are influenced by minerals including nutrient acquisition, cell adhesion and biofilm formation (45). Essential nutrients and environmental contaminants sorbed to mineral surfaces can be acquired or removed by organisms including metals and organic compounds (46,47). Other elements and nutrients may be released from minerals as a result of bioweathering, and fungi have notable activities in this context (3,16,24,48).

Bioweathering can be defined as the erosion, decay and decomposition of rocks and minerals mediated by living organisms. Fungi are well suited as geoactive weathering agents since they possess a variety of growth, metabolic and morphological strategies and can be resistant to a range of environmental extremes such as metal toxicity, UV radiation, and desiccation. Their mutualistic associations with plants (mycorrhizas), algae and cyanobacteria (lichens) are particularly significant geoactive agents (3,16,24,48). The ability of fungi to translocate water, ions and nutrients within the mycelial network is another important feature for exploiting heterogeneous environments (49-51).

Fungi appear to be ubiquitous components of the microbiota of all rocks, building stone and concrete, and have been reported from a wide range of rock types, e.g. limestone, marble, granite, sandstone, basalt, gneiss, dolerite and quartz, even from the most extreme environments (9,16,48). Rock surfaces may be subject to moisture deficit and nutrient limitation although many species can tolerate extremes of UV irradiation, salinity, pH, and water potential (16,24,25,48,52). Nutrients can be scavenged from the atmosphere and rainwater, and they also use organic and inorganic residues on surfaces or within cracks and

fissures, waste products of other microorganisms, decaying plants and insects, dust particles, aerosols and animal faeces as nutrient sources (24). Fungi may receive protection from environmental extremes by the presence of melanin pigments and mycosporines in their cell walls, and by the production of mucilaginous exopolymeric substances that may entrap inorganic particulates, e.g. clay minerals, providing further protection (9,53). Fungal interactions with rock-mineral substrates can result in dissolution and biodeterioration but also the formation of patinas, films, varnishes, and crusts (3,9). In soil, fungus-mineral interactions are also an integral component of environmental cycling of elements and nutrients (4,21).

Biomechanical deterioration of rocks and minerals can occur through hyphal penetration and burrowing into decaying material and along crystal planes in, e.g. calcitic and dolomitic rocks (3,24,54). Intracellular turgor pressure may be a significant factor in biomechanical disruption (55,56). Spatial exploration of the environment to locate and exploit new substrates is facilitated by a range of sensory responses that determine the direction of hyphal growth such as thigmotropism (or contact guidance) (57). Biochemical weathering of rocks and minerals can occur through excretion of geoactive metabolites (58,59), and this is believed to be a more significant process than mechanical degradation although a combination of mechanisms is often likely. This can result in pitting and etching of surfaces to complete dissolution of mineral grains (60-62). Bioweathering is a highly significant process and has direct consequences not only for rock and mineral dissolution, but the mobilization and immobilization of metals, nutrient release, and the formation of secondary minerals (2,3).

Metal mobilization

Metal mobilization from rocks, minerals, soil and other substrates can be a consequence of protonolysis, carbonic acid formation from respiratory CO_2, complexation by Fe(III)-binding

siderophores and other excreted metabolites, e.g. amino acids, phenolic compounds, and organic acids, and methylation (for e.g. Hg, Se and As) which can result in volatilization. Fungal-excreted carboxylic acids can attack mineral surfaces providing protons as well as a metal-chelating anion, e.g. citrate (58). Oxalic acid can leach metals that form soluble oxalate complexes, e.g. Al and Fe (63). Solubilization mechanisms can result in metal mobilization from toxic metal containing minerals, e.g. pyromorphite ($Pb_5(PO_4)_3Cl$), contaminated soil and other solid wastes (64-66). Fungi may also mobilize metals and attack mineral surfaces by redox transformations: Fe(III) and Mn(IV) solubility is increased by reduction to Fe(II) and Mn(II) respectively. Fungal reduction of Hg(II) to volatile elemental Hg(0) has also been recorded (67). As discussed earlier, metals may be mobilized from organic substrates during decomposition (21).

Metal immobilization

Fungi are effective accumulators of metals and related substances. Important mechanisms include biosorption to cell walls, pigments and exopolymers, intracellular transport, accumulation and sequestration, or bioprecipitation on and/or around hyphae (3,53,68-76). Living or dead fungal biomass are effective biosorbents for a variety of metals including Ni, Zn, Ag, Cu, Cd and Pb as well as actinides, e.g. U, Th, with a variety of functional groups being involved (24,53,76). The presence of chitin, and pigments like melanin, may enhance the ability of fungal biomass to act as a biosorbent. Fungal biomineralization processes lead to metal immobilization as biominerals or elemental forms, as described below (3).

Biomineralization

Biomineralization refers to the processes by which organisms form minerals. Biologically-induced mineralization (BIM) is where the organism modifies the local microenvironment

creating conditions amenable for extracellular chemical precipitation of mineral phases. The organism does not appear to control the biomineralization process in BIM while a great degree of control over biomineralization is exerted in biologically-controlled biomineralization (BCM), e.g. the complex cellular biomineral structures found in certain other eukaryotes like diatoms (77). Fungal biomineralization therefore usually refers to biologically-induced mineralization. This can result from the bioweathering mechanisms discussed previously such as redox transformations and metabolite excretion (78,79) and organic matter decomposition where released substances re-precipitate with metals in the microenvironment, and *vice versa* (4,21,80-82). As mentioned, fungal surfaces provide many reactive sites for sorption (≡ biosorption) and this can also lead to the formation of mineral precipitates (2,71,83).

Common Mineral and Biomineral Transformations by Fungi

Fungi are involved in many environmental mineral transformations at differing scales (84-86). They are clearly a very important group of geoactive organisms especially when considering their ubiquity and capacity for production of mineral-transforming metabolites, their symbiotic associations, and the aforementioned consequences of their major significance in organic matter decomposition (4,5).

Carbonates Insoluble carbonates may be broken down by fungal attack, usually the result of acid formation (87-89). Such activity is particularly evident on limestones and marble used in building construction, but can also occur in natural limestone (88,90). Fungal attack on carbonates (dolomites and limestones) can result in transformation of these substrates to dolomite ($CaMg(CO_3)_2$), glushinskite ($MgC_2O_4.2H_2O$), weddellite ($CaC_2O_4.2H_2O$), whewellite ($CaC_2O_4.H_2O$), and possibly struvite ($NH_4MgPO_4 \cdot 6H_2O$) (91).

Certain fungi can deposit calcium carbonate extracellularly (92-95). Calcite ($CaCO_3$) and calcium oxalate monohydrate (whewellite; $CaC_2O_4.H_2O$) was precipitated on hyphae of *Serpula himantioides* when grown in simulated limestone microcosms (93). Urease-positive fungi degrade urea liberating carbonate (96). This process results in the precipitation of metal-containing carbonates which provides a means of metal immobilization and biorecovery (94). Incubation of *Neurospora crassa* in urea-containing media resulted in the formation of calcite, as well as carbonates containing other metals. When a carbonate-laden *N. crassa* culture supernatant was mixed with $CdCl_2$, the Cd was precipitated in the form of highly pure otavite ($CdCO_3$) (94). After incubation in media containing urea and $CaCl_2$ and/or $SrCl_2$, *Pestalotiopsis* sp. and *Xepiculopsis graminea* (syn. *Myrothecium gramineum*), isolated from calcareous soil, precipitated calcite ($CaCO_3$), strontianite ($SrCO_3$), vaterite in different forms [$CaCO_3$, $(Ca_xSr_{1-x})CO_3$] and olekminskite [$Sr(Sr,Ca)(CO_3)_2$] suggesting that urease-positive fungi could play an important role in the environmental fate, bioremediation or biorecovery of Sr or other metals and radionuclides that form insoluble carbonates (95). *Paecilomyces javanicus* mediated the formation of an unknown lead mineral phase after incubation in liquid media with lead shot. After 2 weeks incubation, precipitated mineral phase particles were found to contain plumbonacrite ($Pb_{10}(CO_3)_6O(OH)_6$). However, after 4 weeks incubation, the lead particles that accumulated inside the fungal pellets were transformed into a white mineral phase composed of lead oxalate (PbC_2O_4), hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) and a new lead hydroxycarbonate mineral species, thus revealing novel steps in lead carbonation by fungi (97).

Oxalates Calcium oxalate is the most common form of oxalate in the environment, occurring as the dihydrate ($CaC_2O_4.3H_2O$, weddellite) or the more stable monohydrate ($CaC_2O_4.H_2O$, whewellite) (59,79). Calcium oxalate can be associated with free-living, pathogenic and plant symbiotic fungi, and lichens, and is formed by precipitation of soluble calcium as the oxalate

(59,61,87,98,99). Fungal calcium oxalate can exhibit a variety of crystalline forms (tetragonal, bipyramidal, plate-like, rhombohedral or needles) (100). Calcium oxalate has an important influence on soil biogeochemistry, acting as a calcium reservoir, and can also influence phosphate availability. Fungi can produce many other metal oxalates on interacting with a variety of different metals and metal-bearing minerals, e.g. Ca, Cd, Co, Cu, Mg, Mn, Sr, Zn, Ni and Pb (3,59,64,79,101-103). The formation of toxic metal oxalates may contribute to fungal metal tolerance (53,102). In many arid and semi-arid regions, calcareous soils and near surface limestones (calcretes) are secondarily cemented with calcite ($CaCO_3$) and whewellite (calcium oxalate monohydrate, $CaC_2O_4.H_2O$) and the presence of fungal filaments biomineralized with these substances has been reported (52). Calcium oxalate can also be degraded to calcium carbonate, and this may again cement pre-existing limestones (104). Other experimental work has demonstrated fungal precipitation of secondary calcite, whewellite, and glushkinskite ($MgC_2O_4.2H_2O$) (3,16,48,93). Fungal attack on a dolomitic and seawater substrate resulted in the formation of Ca-oxalates (weddellite, $CaC_2O_4.2H_2O$; whewellite, $CaC_2O_4.H_2O$) and glushinskite ($MgC_2O_4.2H_2O$) (105).

Oxides Several fungi can oxidize Mn(II) to $Mn(IV)O_2$ including *Acremonium* spp. (17,106,107). Fungal oxidation is probably non-enzymatic in many cases although involvement of laccase and/or multicopper oxidases have been shown in ascomycetes (17,106). Non-enzymatic microbial Mn^{2+} oxidation may be effected through production of organic acids such as citrate, lactate, malate, gluconate, or tartrate. Some fungi can oxidize Mn(II) and Fe(II) in metal-bearing minerals such as siderite ($FeCO_3$) and rhodochrosite ($MnCO_3$) resulting in their precipitation as oxides (108). Manganese and iron oxides are major components (20–30%) along with clay (~60%) and various trace elements in desert varnish (9,108). Oxidation of Fe(II) and Mn(II) by fungi can lead to the formation of dark patinas on glass surfaces (109).

Manganese-reducing microbes may mobilize oxidized manganese, releasing it into the aqueous phase. Most of those fungi that reduce Mn(IV) oxides reduce them indirectly (non-enzymatically) with the likely mechanism being the production of metabolic products that act as reductants for Mn(IV) such as oxalate (1,103).

Phosphates Phosphorus occurs primarily as organic phosphate esters and inorganic forms, e.g. calcium, aluminium, and iron phosphates. Organic phosphates are broken down by phosphatases which liberate orthophosphate during the microbial decomposition of organic material. Fungi also mobilize orthophosphate from insoluble inorganic phosphates by producing acids or chelators, e.g. gluconate, citrate, oxalate, and lactate, which complex the metal resulting in dissociation. Phosphate-solubilization is very important in the plant mycorrhizosphere (110). Microbes can also play a role in the formation of phosphate minerals such as vivianite ($Fe_3(PO_4)_2.8H_2O$), strengite ($FePO_4.2H_2O$), and variscite ($AlPO_4.2H_2O$). The orthophosphate may be derived from organic phosphate degradation while Fe or Al may arise from solubilization of other minerals. Such formation of phosphate minerals is probably most common in soil (1). Fungal biodeterioration of metallic lead can result in pyromorphite ($Pb_5[PO_4]_3X$ [X= F, Cl or OH]) formation (111-113). Many fungi can solubilize uranium oxides and depleted uranium and reprecipitate secondary uranium phosphate minerals, uramphite and/or chernikovite, which can encrust fungal hyphae to high accumulation values (73,74,114). These minerals appear capable of long-term U retention (73,74,114,115). *Aspergillus niger* and *Paecilomyces javanicus* precipitated U-containing phosphate biominerals when grown with an organic P source with the hyphal matrix acting to localize the uranium minerals. The uranyl phosphates identified included potassium uranyl phosphate hydrate ($KPUO_6.3H_2O$), meta-ankoleite [$(K_{1.7}Ba_{0.2})(UO_2)_2(PO_4)_2.6H_2O$], uranyl phosphate hydrate [$(UO_2)_3(PO_4)_2.4H_2O$], meta-ankoleite ($K(UO_2)(PO_4).3H_2O$), uramphite

373 ($NH_4UO_2PO_4.3H_2O$) and chernikovite [$(H_3O)_2(UO_2)_2(PO_4)_2.6H_2O$] (80). These organisms
374 could also mediate lead bioprecipitation during growth on organic P substrates (81). These
375 minerals were identified as pyromorphite ($Pb_5(PO_4)_3Cl$) which was only produced by *P.*
376 *javanicus*, and lead oxalate (PbC_2O_4), which was produced by *A. niger* and *P. javanicus* (81).
377 Several yeasts could also mediate lead bioprecipitation when utilizing an organic phosphorus-
378 containing substrate (glycerol 2-phosphate, phytic acid) as sole phosphorus source. The
379 minerals precipitated here included lead phosphate ($Pb_3(PO_4)_2$), pyromorphite ($Pb_5(PO_4)_3Cl$),
380 anglesite ($PbSO_4$), and the lead oxides massicot and litharge (PbO). All yeasts examined
381 produced pyromorphite, and most produced anglesite (82).
382
383 **Silicates** Silicates comprise 30% of all minerals and about 90% of the Earth's crust (116)
384 (1,60,116). Many species of fungi play a role in the dissolution of silicates and therefore in the
385 formation of clay minerals, and in soil and sediment formation (54, 87, 117-122). The presence
386 of clay minerals can be a typical symptom of rock bioweathering by lichens and
387 ectomycorrhizas (118,119). Bioweathering is mainly indirect, through the production of
388 metabolites together with biomechanical effects (123,124). Geoactive metabolites may be
389 excreted into the bulk phase but may also be produced by adhering organisms on silicate
390 surfaces resulting in etching (125,126). After colonization of sheets of muscovite, a
391 phyllosilicate mineral, by *Aspergillus niger*, dissolution was evident by a network of fungal
392 "footprints" that reflected coverage by the mycelium (126). New biominerals resulted from
393 fungal interactions with both zinc silicate and zinc sulfide, largely resulting from organic acid
394 excretion. Zinc oxalate dihydrate was formed and mineral surfaces showed varying patterns of
395 bioweathering and biomineral formation (127). Silicate dissolution may release limiting
396 nutrients like bound P and Fe. In lichen bioweathering of silicates, calcium, potassium, iron,
397 clay minerals and nanocrystalline aluminous iron oxyhydroxides become mixed with fungal

organic polymers (118), while biotite ($K(Mg,Fe(II))_3AlSi_3O_{10}(OH,O,F)_2$) was penetrated by fungal hyphae along cleavages, partially converting it to vermiculite ($((Mg,Fe(II),Al)_3(Al,Si)_4O_{10}(OH)_2.4H_2O$) (117). The fungal partner has also been reported to be involved in formation of secondary silicates, such as opal ($SiO_2.nH_2O$) and forsterite (Mg_2SiO_4), in lichen thalli (128). The transformation rate of mica and chlorite to clay minerals was pronounced in ectomycorrhizosphere soil and probably a result production of organic acids and direct extraction of K^+ and Mg^{2+} by fungal hyphae (119). Fungal-clay mineral interactions also play an important role in soil development, aggregation and stabilization (16,129). Interactions between clay minerals and fungal biomass alters the sorptive properties of both clay minerals and fungal hyphae (130,131) and also affect the size, shape and structure of mycelial pellets (132).

Reduction or oxidation of metals and metalloids Many fungi can precipitate reduced forms of metals and metalloids, e.g. Ag(I) reduction to elemental silver Ag(0); selenate [Se(VI)] and selenite [Se(IV)] to elemental selenium [Se(0)]; tellurite [Te(IV)] to elemental tellurium [Te(0)] (133-135). Reduction of Hg(II) to volatile Hg(0) can also be mediated by fungi (67,68). Increased arsenate reduction contributed to tolerance in an *Aspergillus* sp. (136,137). Mn oxidation/reduction has been described above.

Other mycogenic minerals A range of minerals other than those mentioned above have been found in association with fungi (2,3,73,74,77,80-82,114). Mycogenic secondary minerals associated with fungal hyphae and lichen thalli include desert varnish (MnO and FeO), ferrihydrite ($5Fe_2O_3.9H_2O$), iron gluconate, calcium formate, forsterite, goethite (α-$Fe^{3+}O(OH)$), moolooite ($Cu(C_2O_4).0.4H_2O$), halloysite ($Al_2Si_2O_5(OH)_4$), and hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) (16,48,52,108,120,128,138). Another biogenic mineral (tepius) has been

identified in association with a lichen carpet occurring in high mountain ranges in Venezuela (128).

Halide transformations Several fungi have the ability to produce a variety of atmospheric methyl halides. This ability is widespread in both free-living and symbiotic fungi, and is dependent on substrate concentration and community composition (139,140). The production of chloromethane (CH_3Cl) by wood-rotting fungi, e.g. *Phellinus* spp., may be particularly significant with one estimate of annual global input to the atmosphere from this source being 160 000 t of which 75% is released from tropical and subtropical forests (139). Filamentous fungi may also contribute to the global circulation of stable iodine and also the long-lived radioiodine, ^{129}I (half-life: 1.6×10^7 years), released from nuclear facilities (141).

FUNGAL SYMBIOSES IN GEOMYCOLOGY

Many fungi form partnerships with plants (mycorrhizas) and algae or cyanobacteria (lichens) that are significant geoactive agents. In general terms, the mycobiont is provided with carbon by the photobionts, while the mycobiont may protect the symbiosis from harsh environmental conditions (e.g., desiccation, metal toxicity), and provide increased access to inorganic nutrients such as phosphate and essential metals.

Lichens are fungi that exist in facultative or obligate symbioses with one or more photosynthesizing partners occurring in almost all surface terrestrial environments (142). Lichens play important roles in retention and distribution of nutrient (e.g. C, N) and trace elements, in soil formation, and rock bioweathering (54,87,143). Lichens can accumulate metals such as lead (Pb) and copper (Cu), and many other elements, including radionuclides (144). They also form a variety of metal-organic biominerals, e.g. oxalates, especially during

448 growth on metal-rich substrates (98,143). On copper sulfide bearing rocks, precipitation of
449 copper oxalate (moolooite) can occur within lichen thalli (145,146).
450
451 The majority of terrestrial plants depend on symbiotic mycorrhizal fungi (147,148).
452 Mycorrhizal fungi can mediate metal and phosphate solubilization from mineral sources,
453 extracellular precipitation of metal oxalates, and immobilize metals within biomass
454 (65,66,149-157). Such activities lead to changes in the physico-chemical characteristics of the
455 root environment and enhanced bioweathering of soil minerals (55,157,158). Furthermore,
456 ectomycorrhizal mycelia may respond to different soil silicate and phosphate minerals (e.g.
457 apatite, quartz, potassium feldspar) by regulating growth and metabolic activity (159,160).
458
459 Mycorrhizal fungi often excrete bioweathering agents such as low molecular weight
460 carboxylic acids and siderophores (65,161). Ectomycorrhizal fungi can also form narrow
461 pores in weatherable minerals in podzol E horizons, probably by dissolution of Al silicates
462 (162,163). Such excretions can also release elements from apatite and wood ash (K, Ca, Ti,
463 Mn, Pb) (164). Ericoid mycorrhizal and ectomycorrhizal fungi can dissolve several
464 cadmium, copper, zinc and lead-bearing minerals including metal phosphates
465 (65,66,152,161,165). Mobilization of phosphorus from inorganic and organic phosphorus
466 sources is generally regarded as one of the most important functions of mycorrhizal fungi,
467 and this can also result in redistribution of incorporated metals, and the formation of other
468 secondary minerals including other metal phosphates. The ericoid mycorrhiza *Oidiodendron*
469 *maius* can solubilize zinc oxide and phosphate (161). Many ericoid mycorrhizal and
470 ectomycorrhizal fungi are able to solubilize zinc, cadmium, copper phosphates and lead
471 chlorophosphate (pyromorphite) releasing phosphate and component metals (65,152). An
472 association of arbuscular mycorrhizal fungi (AMF) with *Lindenbergia philippensis*, sampled

from a Zn-contaminated settling pond at a zinc smelter, enhanced Zn accumulation in Zn-loaded rhizosphere sediment compared to treatments that suppressed AMF colonization. A significant proportion of Zn was present as crystalline and other solid materials that were associated with the root mucilaginous sheath (166). Such results may indicate a role for AMF in enhancing Zn immobilization in the rhizosphere of plants that successfully colonize Zn mining and smelting disposal sites (153,166,168).

ENVIRONMENTAL AND APPLIED SIGNIFICANCE OF GEOMYCOLOGY

The kinds of processes detailed previously can impact upon human society not only through their environmental significance and biotechnological applications, but also in deleterious contexts such as biodeterioration and biocorrosion. The biodeterioration of stone and mineral artefacts represents a loss of cultural heritage (13,14). Materials used to stabilize building blocks (mortar) and to coat surfaces prior to painting (plaster or stucco) are also susceptible to biodeterioration (13). Highly deteriorated stone surfaces provide a ‘‘proto-soil’’ for colonization by mosses, ferns and higher plants (14). Mechanisms of stone deterioration are complex and include most of the direct and indirect mechanisms previously discussed for mineral dissolution (13,169). Extracellular polymeric substances (EPS) are also capable of metal complexation and weakening of mineral lattices through wetting and drying cycles, as well as the production of efflorescences, i.e. secondary minerals produced through reaction of anions from excreted acids with cations from the stone (170). Physical damage may be caused by hyphal penetration of weakened areas (88,138). Lichens cause damage due to penetration by their rhizines, composed of fungal filaments, and expansion/contraction of the thallus on wetting/drying (171). ‘‘Lichen acids’’, mainly oxalic acid, cause damage at the stone/lichen interface, and lichen thalli may accumulate up to 50% calcium oxalate, depending on the substrate (172,173). In addition, carbonic acid formed in the lichen thallus

can solubilize calcium and magnesium carbonates in calcareous stone (174). Fungal biodeterioration of ancient ivory (natural apatite; walrus tusk) was accompanied by widespread etching and tunneling by hyphae and extensive formation of calcium oxalate monohydrate, whewellite (175). Concrete and cement can be biodeteriorated and in some environments, fungi dominate the concrete-deteriorating microbiota (13,14,176-178). Microbial attack on concrete is mediated by protons, inorganic and organic acids and the production of hydrophilic slimes leading to biochemical and biomechanical deterioration (13,75,169). Several species of microfungi were able to colonize samples of the concrete used as radioactive waste barrier in the Chernobyl reactor and leached iron, aluminium, silicon and calcium, and re-precipitated silicon and calcium oxalate (75).

Mineral and metal solubilization mechanisms enable metal removal from industrial wastes, low-grade ores, and metal-bearing minerals. This may have application in bioremediation, metal biorecovery and recycling (58,68,179,180). Metals can be solubilized from fly ash (originating from municipal solid waste incineration), contaminated soil, electronic scrap and other waste materials by fungal activity (179,181). Although fungal systems cannot compare with the efficiency of bacterial bioleaching, they may be more suited to specific bioreactor applications (58). A variety of fungal mechanisms result in metal immobilization such as biosorption, bioaccumulation and bioprecipitation. Biosorption is a physico-chemical process, and is a property of both living and dead organisms (and their components), and fungi are effective agents for removal of metals, radionuclides and other substances from solution (69,70,71,76,130,182-193). Urease-positive fungi can be used to precipitate metal-containing carbonates, some in nanoscale dimensions, thus providing a means of metal biorecovery as well as potentially useful nanoscale biomineral products (94,95). Similarly, the formation of other insoluble metal compounds by fungi or their metabolites could also be

considered as a means to biorecover metals, metalloids and radionuclides, e.g. oxalates, oxides, oxalates, and phosphates, as well as the production of elemental metal or metalloid forms (2,78). Some biomineral and elemental products, including those of nanoscale dimensions, are of relevance to the production of novel advanced biomaterials with applications in metal and radionuclide bioremediation, antimicrobial treatments (e.g. nano-silver), solar energy and electrical battery applications, and microelectronics (194). In a novel approach, urease-positive *Neurospora crassa* was used to precipitate manganese carbonate. After thermal treatment at 300^{o}C, the carbonized biomass-manganese oxide composite material was used in lithium-ion batteries (LiB) and supercapacitors where it was found to exhibit excellent electrochemical properties. In LiB, around 90% charge capacity was retained after 200 charge-discharge cycles (195).

The ability of fungi and bacteria to transform metalloids has been successfully used for bioremediation of contaminated land and water. Selenium methylation results in volatilization and this has been used to remove selenium from the San Joaquin Valley and Kesterson Reservoir, California (196). Mycorrhizal associations may have application in phytoremediation (197,198), the use of plants to remove or detoxify environmental pollutants (199), by metal phytoextraction or by acting as a biological barrier (200-202). Glomalin, an insoluble glycoprotein, is produced in copious amounts on hyphae of arbuscular mycorrhizal fungi and can sequester metals such as Cu, Cd and Pb (203). Arbuscular mycorrhizal fungi can also decrease U translocation from plant roots to shoot (204-206). For ericaceous mycorrhizas, the fungus prevents translocation of Cu and Zn to host plant shoots (147,207,208). The development of stress-tolerant plant-mycorrhizal associations may be a promising strategy for phytoremediation and soil amelioration (161,209,210).

548 Some of the geomycological processes detailed previously may have consequences for
549 abiotic soil treatment processes, notably the immobilization of toxic metals by phosphate
550 formation. Apatite $Ca_5(PO_4)_3(F,Cl,OH)$, pyromorphite $Pb_5(PO_4)_3Cl$, mimetite
551 $Pb_5(AsO_4)_3Cl$ and vanadinite $Pb_5(VO_4)_3Cl$ are the most common prototypes of the apatite
552 mineral family. Such minerals hold promise for stabilization and recycling of industrial and
553 nuclear waste and have been explored for treatment of lead-contaminated soils and waters
554 (211-216). The stability of these minerals is therefore of interest in any soil remediation
555 strategy seeking to reduce the effects of potentially-toxic elements, like Pb, V and As. For
556 example, pyromorphite is a highly insoluble lead phosphate mineral under a wide range of
557 geochemical conditions and has often been suggested as a means to reduce Pb bioavailability.
558 However, solubilization of pyromorphite and formation of lead oxalate by several free-living
559 and symbiotic fungi demonstrates that pyromorphite may not be as effective at immobilizing
560 lead as some previous studies have suggested (64,65). Similarly, despite the insolubility of
561 vanadinite, fungi exerted both biochemical and biophysical effects on the mineral including
562 etching, penetration and the formation of new biominerals (217). Lead oxalate was
563 precipitated by *Aspergillus niger* during the bioleaching of vanadinite and mimetite which
564 implies a general fungal mechanism for the transformation of lead-containing apatite group
565 minerals (e.g. vanadinite, pyromorphite, mimetite) (217,218). This pattern of fungal
566 bioweathering of lead apatites could be extended to other metal apatites, such as calcium
567 apatite [$Ca_5(PO_4)_3(OH,F,Cl)$]. Here, the formation of monohydrated (whewellite) and
568 dihydrated (weddellite) calcium oxalate can be accomplished by many different fungal
569 species (79,93,99,175,219,220). The ability of free-living and mycorrhizal fungi to transform
570 toxic metal-containing minerals should therefore be taken into account in risk assessments of
571 the long-term environmental consequences of *in situ* chemical remediation techniques,
572 revegetation strategies or natural attenuation of contaminated sites. The bioweathering

potential of fungi has been suggested as a possible means for the bioremediation of asbestos rich soils. Several fungi could extract iron from asbestos mineral fibres (e.g. 7.3% from crocidolite and 33.6% from chrysotile by a *Verticillium* sp.), thereby removing the reactive iron ions responsible for DNA damage (221).

CONCLUSIONS

The geoactive roles of fungi have often received scant attention in geomicrobiological contexts but they are of clear importance in several key areas. These include a variety of organic and inorganic transformations important in nutrient and element cycling, rock and mineral bioweathering, mycogenic biomineral formation, and metal-fungal interactions. Lichens and mycorrhizas are of special significance as geoactive agents. Organic matter decomposition is important for the cycling of major biomass-associated elements, e.g. C, H, N, O, P and S as well as all other elements that may be found in lower concentrations. Transformations of metals and minerals are central to many geomicrobial processes, and fungi can effect changes in metal speciation, toxicity and mobility, as well as mediate mineral formation or dissolution. Such mechanisms are important components of natural biogeochemical cycles for metals as well as associated elements in biomass, soil, rocks and minerals, e.g. S and P, and metalloids, actinides and metal radionuclides. It is within the terrestrial environment where fungi have the greatest abundance and geochemical influence. However, they are also important in aquatic habitats and are now recognized as significant components of aquatic sediments and the deep subsurface. Geomycological processes can have beneficial or detrimental consequences in a human context. Beneficial applications in environmental biotechnology include metal and radionuclide bioleaching, biorecovery, detoxification, and bioremediation, and in the production of biominerals or metal(loid) elements with catalytic or other properties in nanoparticle, crystalline or colloidal forms. The

latter may be relevant to the development of novel biomaterials. Adverse effects include biodeterioration and destruction of natural and synthetic materials, rock and mineral-based building materials (e.g. concrete), cultural heritage, biocorrosion of metals, alloys and related substances, and adverse effects on radionuclide speciation, mobility and containment. The ubiquity and importance of fungi in biosphere processes underlines the importance of geomycology as a conceptual framework encompassing the environmental activities of fungi, their impact, and their applied significance.

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